ON GRAPHITE PARTICLES AS INTERSTELLAR GRAINS

F. Hoyle and N. C. Wickramasinghe

Summary

The interstellar reddening curve predicted theoretically for small graphite flakes is in remarkable agreement with the observed reddening law, suggesting that the interstellar grains may be graphite and not ice. This possibility is not in contradiction with the high albedos of reflection nebulae at photographic wave-lengths, provided the particles have sizes of order 10^{-5} cm.

The origin of graphite flakes at the surfaces of cool carbon stars is considered, about 10^4 N stars in the galaxy being sufficient to produce the required density of interstellar grains in a time of 3×10^9 years.

Grains tend to be formed in the pulsation cycle of an N star at temperatures $< 2700°$K. The grains have an important effect on the photospheric opacity, causing the photospheric density to decrease very markedly as the temperature falls towards $2000°$K. It is this fall of density that allows the grains to be repelled outwards by radiation pressure and to leave the star altogether in spite of the frictional resistance of the photospheric gases. The grains do not evaporate as they leave the atmosphere of the star.

Much of the empirical data concerning graphite is uncertain. The optical constants used in deriving the reddening law are consistent, however, with the reflectivity of polished graphite surfaces. A low value of 10^{-3} has been used for the accommodation coefficient, since this has been obtained in the most extensive series of experiments. With this value it is shown that the expelled grains can reach a size of $\sim 10^{-5}$ cm. The velocities of expulsion from stars can exceed 1000 km sec^{-1}.

The possibility that interstellar grains are carbon particles produced by stars has important cosmogonic consequences. Grains can be produced in galaxies that contain little or no gas. Grains can be expelled from galaxies. Graphite is highly refractory and would not evaporate in H II regions. Graphite chemisorbs hydrogen and is therefore an effective catalyst in the production of interstellar H_2. Indeed, graphite grains would be highly efficient in the production of interstellar molecules in general, whereas ice is probably very inefficient. Graphite possesses anisotropic conductivity and this may be important in the phenomenon of interstellar polarization, as has been suggested by Schatzman and Cayrel, and also, more recently, by Wickramasinghe.

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1. *Introduction.*—To explain the observed interstellar extinction, about 1 mag per kpc at 4000 Å, the average mass density of interstellar grains must be remarkably high. Even for particles of the most efficient size, the mass density cannot be much less than 10^{-26} gm cm^{-3}. Since the total average density of the whole interstellar medium is not greater than about 5×10^{-24} gm cm^{-3}, of the order of one part in 500 of the medium must exist in the form of grains.

Goldberg, Müller and Aller (**1**) give the following relative abundances for the Sun: $H = 3 \cdot 2 \times 10^{10}$, $C = 1 \cdot 7 \times 10^7$, $O = 2 \cdot 9 \times 10^7$, $Mg = 8 \times 10^5$, $Si = 10^6$,

Fe $= 1\cdot2 \times 10^5$. For interstellar material of similar composition it is clear that only C and O would be present in sufficient concentrations to provide the main contribution to the grain density. Oxygen combined with hydrogen could be condensed as ice crystals, whereas carbon could be present in free form as graphite crystals. Of these possibilities, the first has usually been considered the more likely. The present paper seeks to consider the evidence and arguments in favour of the second possibility.

Graphite crystals do not behave as dielectric particles. Good quality graphite possesses a low frequency conductivity of $\sim 10^{16}$ sec^{-1}. At optical frequencies the conductivity is likely to be less than this, but a value $\sim 10^{15}$ sec^{-1} is entirely possible, and this, being $\sim c/\lambda$, has an important effect on the extinction and albedo properties of such crystals. Unfortunately good values for the optical constants of graphite are not available. However, evidence from the normal reflectivity of a polished plane graphite surface does support the view that the optical conductivity σ is $\sim 10^{15}$ sec^{-1}. The coefficient of reflection R is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2},\tag{1}$$

$$n^2 = \tfrac{1}{2}[(K^2 + 4\sigma^2\lambda^2/c^2)^{1/2} + K],\tag{2}$$

$$k^2 = \tfrac{1}{2}[(K^2 + 4\sigma^2\lambda^2/c^2)^{1/2} - K],\tag{3}$$

where K is the dielectric constant—probably close to 2 for a substance with the density of graphite ($2\cdot2$ gm cm^{-3}). For $K=2$, $\sigma = 10^{15}$ sec^{-1}, these formulae give reflectivities of $0\cdot175$ at $\lambda = 0\cdot5\,\mu$, $0\cdot306$ at $\lambda = 1\,\mu$, $0\cdot706$ at $\lambda = 10\,\mu$. The corresponding experimental values are $0\cdot22$, $0\cdot27$, $0\cdot59$ respectively (2). The latter data, being rather old, are probably not very accurate—modern techniques using evaporated metal surfaces sometimes give appreciable differences from results obtained with polished surfaces. Nevertheless, the quite good agreement between calculation and observation gives support to the values we shall use in the following section, $K=2$, $\sigma = 1\cdot2 \times 10^{15}$ sec^{-1}. Moreover, old experiments (3) on the scattering of light by small carbon particles give $m = n - ik = 1\cdot59 - 0\cdot66i$ at $\lambda = 0\cdot491\,\mu$, while the above formulae give $m = n - ik = 1\cdot72 - 0\cdot97i$ at $\lambda = 0\cdot5\,\mu$, again a tolerable agreement, particularly in view of the known variability of different graphite samples.

2. *The interstellar extinction.*—For simplicity, we shall begin by regarding the graphite crystals as spheres possessing isotropic conductivity. The extinction cross-section of a grain of radius a can be written as $\pi a^2 Q(a, \lambda)$. For sufficiently small grains (4)

$$Q(a, \lambda) = \frac{8\pi a}{\lambda}\, \mathrm{Im}\, \frac{1 - m^2}{2 + m^2},\tag{4}$$

with

$$m^2 = K - 2i\sigma\lambda/c.\tag{5}$$

For $K=2$, $\sigma = 1\cdot2 \times 10^{15}$ sec^{-1}, λ in microns,

$$Q = \frac{3\pi a \sigma}{c} \cdot \frac{1}{1 + 4\lambda^2}.\tag{6}$$

The mass absorption coefficient is obtained by dividing the cross-section $\pi a^2 Q(a, \lambda)$ by the mass $\frac{4}{3}\pi a^3 s$ of the grains, where s is their specific gravity. The result for $s = 2\cdot2\,\text{gm cm}^{-3}$ is $1\cdot28 \times 10^5 [1 + 4\lambda^2]^{-1}\,\text{cm}^2\,\text{gm}^{-1}$. To obtain an extinction of 1 mag at $\lambda = 0\cdot4\,\mu$ we require $\sim 10^{-5}\,\text{gm cm}^{-2}$. This mass of grains, distributed along a column of length 1 kpc, gives a space density of $\sim 3 \times 10^{-27}\,\text{gm cm}^{-3}$, somewhat less than the value $\sim 10^{-26}\,\text{gm cm}^{-3}$ quoted above, which applies to the case of ice crystals.

The observed intensity of any object at wave-length λ can be written in the form

$$A(\lambda) \exp\left[-B(1 + 4\lambda^2)^{-1}\right], \qquad (7)$$

where $A(\lambda)$ depends on the intrinsic emission of the object, and B on the quantity of absorbing matter along the line of sight, it being assumed that the grains are small enough for (4) to be used. Thus the change in apparent magnitude, $\Delta m(\lambda)$, due to the presence of the absorbing matter, can be expressed as

$$\Delta m(\lambda) = -1\cdot086 B(1 + 4\lambda^2)^{-1}, \qquad (8)$$

and

$$\Delta m(\lambda) - \Delta m(\lambda_0) = 1\cdot086 B\left[(1 + 4\lambda_0^2)^{-1} - (1 + 4\lambda^2)^{-1}\right], \qquad (9)$$

where λ_0 is some reference wave-length. To compare with the observed extinction we take $\lambda_0^{-1} = 0\cdot99$, and we choose B such that $\Delta m(\lambda) - \Delta m(\lambda_0) = 1\cdot00$ when $\lambda^{-1} = 2\cdot4$. Equation (9) then gives the following values:

TABLE I

λ^{-1}	$\Delta m(\lambda) - \Delta m(\lambda_0)$
0·6	−0·29
0·99	0·00
1·2	0·17
1·4	0·34
1·6	0·49
1·8	0·64
2·0	0·77
2·2	0·89
2·4	1·00
2·6	1·10
2·8	1·18
3·0	1·26

These are plotted in Fig. 1 in a way that can immediately be compared with the results of Whitford (5), shown in Fig. 2. The agreement is manifestly very good. It is perhaps significant that the difference between the figures is greatest at the dotted portion of Whitford's curve ($\lambda > 2\,\mu$) which is simply an extrapolation of the results at shorter wave-lengths.

It is also of interest that the form of Fig. 1 is independent of the sizes of the carbon grains, provided only that they are small enough. The calculated curve is determined by the values of σ, K. Hence if the particles are always small enough the law of interstellar reddening should everywhere be the same.
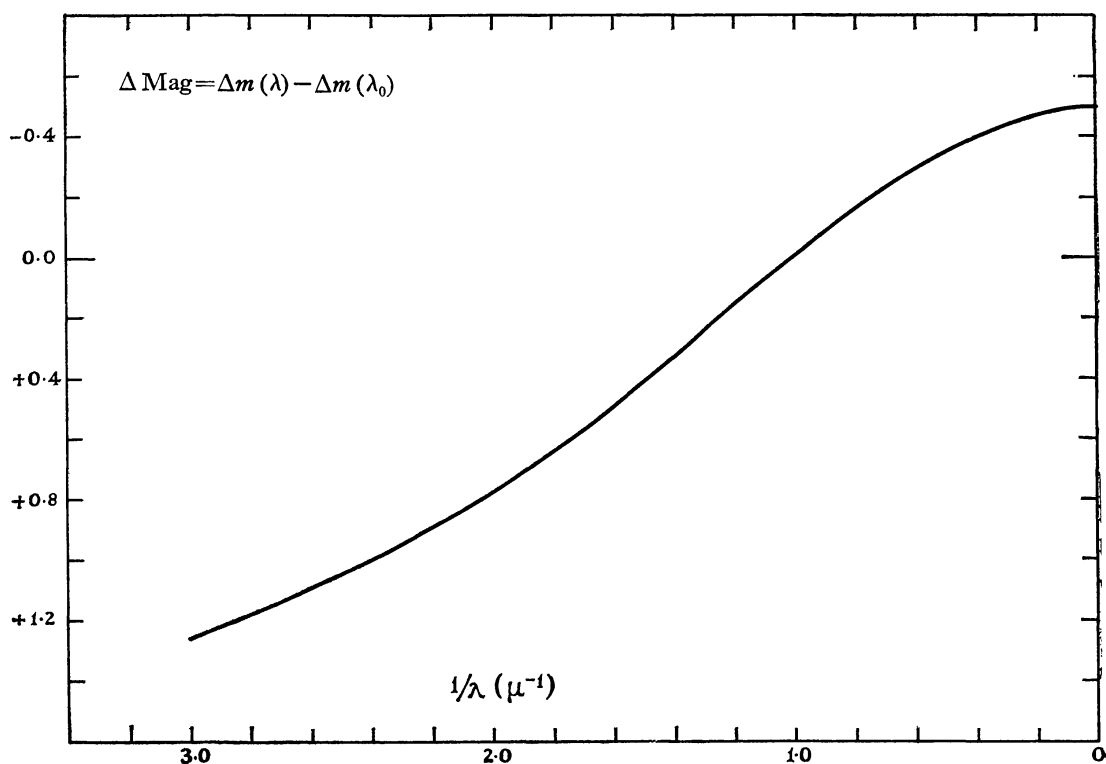
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$$\Delta\,\mathrm{Mag} = \Delta m\,(\lambda) - \Delta m\,(\lambda_0)$$

$$\frac{1}{\lambda}\;(\mu^{-1})$$

FIG. 1.—*Theoretical curve of interstellar reddening.*

ΔMag.

●Scanner   3 stars
○PbS   5 stars

'47 mean
ζ Per '48–'49
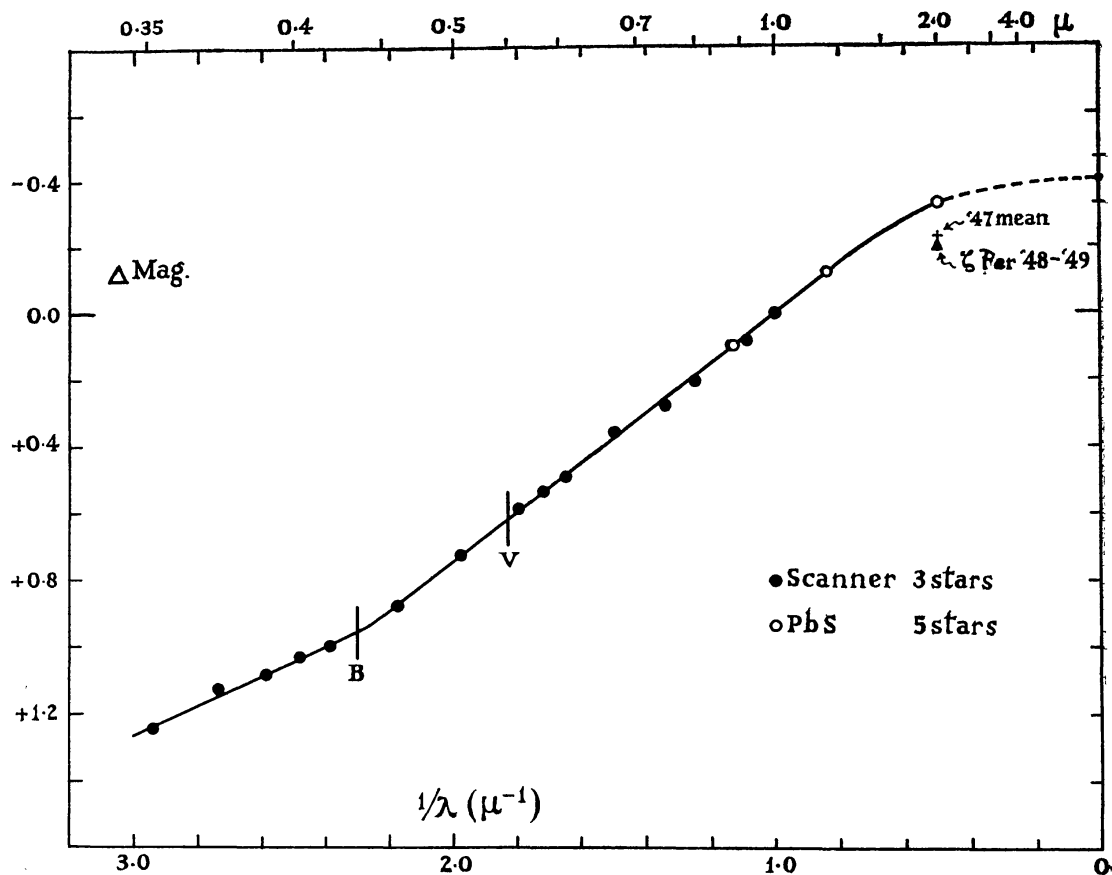
V

B

$$\frac{1}{\lambda}\;(\mu^{-1})$$

FIG. 2.—*Normalized interstellar reddening curve derived from photoelectric scanner observations, and from infra-red filter observations with a lead sulphide photo-conductive cell.*

The restriction on particle sizes arises because the expression (4) for $Q(a, \lambda)$ is only the first term of an infinite series in ascending powers of $2\pi a/\lambda$. Convergence becomes worse as $2\pi a/\lambda$ increases, i.e. as λ decreases for a given a. Hence for a given set of particles the situation is most critical at the shortest wave-length under consideration, $\lambda = \frac{1}{3}\mu$ in the above work. The coefficients in the series depend on m^2. For $K = 2$, $\sigma = 1\cdot2 \times 10^{15} \sec^{-1}$, $m^2 = 2 - 8i\lambda = 2 - 8i/3$ at $\lambda = \frac{1}{3}\mu$. This corresponds to $m = 1\cdot63 - 0\cdot82i$. Now accurate numerical computations have been made by Johnson, Eldridge and Terrell (**6**) for the case $m = 1\cdot29 - 0\cdot64i$. These show that the simple form (4) for Q gives a very good approximation up to a surprisingly large value of $2\pi a/\lambda$, up to $1\cdot5$. Our case can hardly be much different. Thus putting $2\pi a/\lambda \leqslant 1\cdot5$, $\lambda = \frac{1}{3}\mu$, our work is likely to be valid for particles with radii a up to $\sim 8 \times 10^{-6}$ cm.

We turn now to structural questions. Graphite is built from a set of parallel planes, the basal planes. In each plane the carbon atoms are arranged in hexagons, like a honeycomb. Because of its structure it is unlikely that graphite will exist as spherical crystals, rather would one expect plate-like flakes. Although the formulae used above are no longer strictly correct for flakes, we expect their general behaviour to be correct. The restriction on a translates into a restriction on the diameter d, $d < 2a \simeq 1\cdot6 \times 10^{-5}$ cm.

More important, graphite does not possess isotropic conductivity. The conductivity perpendicular to the basal planes is less than that for directions parallel to the planes, by a factor of at least ten. Indeed, for light polarized with the electric vector perpendicular to the basal planes, graphite would behave essentially as a dielectric. The corresponding Q value would be markedly less than that given above. However, for light passing through a medium in which the graphite flakes are randomly orientated the effect will only be to reduce the mass absorption coefficient by a factor between $0\cdot5$ and 1. There will be no important effect on the wave-length dependence, and there will be no polarization effect. But if the flakes are systematically orientated, there will be a strong polarization effect on light that travels in a direction parallel to the basal planes, a feature that has been observed by Schatzman and Cayrel (**9**), and discussed in detail by Wickramasinghe (**10**). Extinction in this case will be largely confined to the component of polarization having the electric vector parallel to the basal planes. These remarks show that if graphite crystals in the interstellar medium tend to be orientated with their normals parallel to what is usually taken to be the direction of the local spiral arm there will be a strong polarizing effect that agrees with the usual discussions. It is emphasized that, just as with the law of reddening, the polarization arises from the basic physical properties of graphite, not from special choices of sizes and shapes for the crystals.

3. *The albedos of reflecting nebulae.*—It has been argued in favour of the ice crystal theory that the high albedos obtained by Hubble (**7**) for reflecting nebulae cannot be explained by conducting particles. While this is true for the iron grains considered by Schalén (**8**), it is not correct for carbon grains, at any rate for the photographic wave-lengths used by Hubble.

For convenience, we again work with spherical particles of isotropic conductivity. The albedo γ is given by

$$\gamma = \tfrac{2}{3}x^3 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \Big/ \mathrm{Im}\left(\frac{1 - m^2}{m^2 + 2}\right), \qquad (10)$$

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for sufficiently small particles (**4**). With $m^2 = 2 - 8i\lambda$, this becomes

$$\gamma = \left(\frac{2\pi a}{\lambda}\right)^3 \frac{1 + 64\lambda^2}{36\lambda} \simeq \frac{16\lambda}{9}\left(\frac{2\pi a}{\lambda}\right)^3. \qquad (11)$$

The above considerations permit a to be large enough for $2\pi a/\lambda \simeq 1$ at photographic wave-lengths, so that $\gamma \simeq 16\lambda/9$—i.e. $\gamma \simeq 0\cdot7$ at $\lambda = 0\cdot4\,\mu$. The essential point is that the simple formula (4) continues to give a good approximation for values of $2\pi a/\lambda$ that even exceed unity. It is this feature that permits a large enough value of the albedo. However, we do require now that the graphite crystals should in the main possess sizes that are not much less than our upper limit—we require overall dimensions of $\sim 10^{-5}$ cm.

A difference arises between graphite and ice crystals at long wave-lengths. The albedo of ice crystals remains high, whereas that of graphite falls off as λ^{-2}. At first sight one might expect that this behaviour would always require a reflection nebula to be bluer than the illuminating star—i.e. than the illuminating star would be if it were unreddened—but this is not so. To consider this point it is necessary to separate the total extinction, which behaves essentially as λ^{-1}, from the scattering which behaves as λ^{-3}. We confine attention to quanta that escape from the nebula. Let λ_b, λ_r be typical blue and red wave-lengths. Suppose that a typical quantum at λ_r experiences N scatterings, $N > 1$. Then a typical quantum at λ_b will experience $N(\lambda_r/\lambda_b)^6$ scatterings. For each scattering at λ_r the light intensity is weakened by γ_r, the albedo at λ_r, while for each scattering at λ_b the intensity is weakened by the corresponding γ_b. The red light is therefore weakened by the factor γ_r^N, whereas the blue light is weakened by $\gamma_b^{N(\lambda_r/\lambda_b)^6}$. Hence with $\gamma \propto \lambda^{-2}$ the ratio of these factors is

$$\frac{\gamma_b^N (\lambda_b/\lambda_r)^{2N}}{\gamma_b^{N(\lambda_r/\lambda_b)^6}} = \left[\left(\frac{\lambda_b}{\lambda_r}\right)^2 \gamma_b^{1 - (\lambda_r/\lambda_b)^6}\right]^N. \qquad (12)$$

Putting $\lambda_b = 0\cdot4\,\mu$, $\lambda_r = 0\cdot6\,\mu$, $\gamma_b = 0\cdot7$, the quantity in the brackets is about 18, showing that the blue light is very heavily attenuated whenever a nebula is opaque enough for N to be of order unity, or more. Although the attenuation is less *per scattering* at λ_b than at λ_r, the number of scatterings at λ_b is greater by the *square* of the ratio of the scattering cross-sections, giving $(\lambda_r/\lambda_b)^6 \simeq 10$.

These considerations apply only for nebulae that are opaque enough for the scattering to be appreciable at λ_r. In less opaque clouds the situation is entirely opposite. For nebulae in which the scattering probability is of order unity at λ_b, the blue light is not much weakened and there is only a small reflection of red light. Such nebulae can appear very blue, bluer than the illuminating star. But as the opacity increases the number of scatterings of the blue light increases very rapidly and at each scattering a fraction of order $0\cdot3$ of the light is lost through absorption. The effect is to produce a sharp quenching of the blue light.

Ice grains do not have this property. The albedo is near unity both at λ_b and λ_r. The scattering behaves as λ^{-1}, so that the number of scatterings in the blue is only about twice that in the red. Unless $N \gg 1$, there is accordingly little loss of light, either at λ_b or λ_r. The whole light, nebula plus star, therefore preserves its original colour. Since the star is reddened, the nebula must be bluer than the unreddened star, although the reflected light may differ with direction according to the position of the star relative to the nebula. In particular directions the reflected light can be reddened, but this cannot be true for the whole of the reflected light.

This difference between ice and graphite could be used to test the two theories. Once again the available data (**11**) are rather old and are limited to a few cases. However, nebulae much redder than the normal colour of the illuminating stars have been found, which tends to support the graphite theory. Much more extensive modern data are evidently needed.

4. *The origin of graphite flakes.*—Contradictory data concerning the accommodation coefficient of gaseous carbon atoms at a graphite surface stand in the way of a theory of the origin of carbon grains. Values of order unity have been quoted in the literature, although probably the most extensive set of experiments, by Doehaerd, Goldfinger and Waelbroek (**12**), gave a result as low as 10^{-3}. In the following, this latter value will be used.

A low value of the accommodation coefficient requires that the grains are not produced in interstellar space, since the growth rate would be much too slow, except possibly in very dense clouds. This in itself is no disadvantage, for an interstellar process would not seem likely to produce the restricted range of grain sizes required by albedo properties and by the reddening law.

The alternative to an interstellar process is one of condensation at stellar surfaces and of expulsion into space by radiation pressure. Such a process was considered some time ago by O'Keefe (**13**). The problem will be rediscussed in the following sections, partly because our interests are different from O'Keefe's, and partly because better thermochemical data are now available (**14**). In particular, we shall use ~ 170 kcal per mole for the heat of evaporation of graphite, instead of the ~ 125 kcal per mole that was thought the more likely value at the time of O'Keefe's paper.

Besides showing that carbon grains can form at stellar surfaces and that they can be expelled into space it is necessary to show that their sizes are of order 10^{-5} cm, and that their amount is sufficient to explain the required interstellar grain density. In the latter connection, only cool giants with spectra dominated by bands of C_2, CN, CH are appropriate sources. Giants showing TiO or ZrO presumably have an excess concentration of O over C. In such stars the carbon must be largely combined as CO, and is not therefore available for forming solid particles. In the carbon stars, on the other hand, C must be more abundant than O, so that, although CO is also present, there is an available excess of carbon. These requirements severely limit the number of stars that are available for grain formation. And of the two types of carbon star we shall find that type N makes a considerably greater contribution than type R. Wilson (**15**) gives about a hundred N stars within 1 kpc of the Sun. Throughout the whole Galaxy there are probably not more than 10^4 such stars, an estimate that also agrees with the more recent work of Nassau and Blanco (**15**). It is necessary to show that this is a sufficient number to provide for the required grain density.

We shall be concerned with stars with surface temperatures that fall in the general range $\sim 2000\,°$K to $2700\,°$K; in fact, with stars that pulsate and which cover this range in their effective temperatures. It will turn out that carbon grains make a large contribution to the photospheric opacity except possibly near maximum phase, the grains giving an optical depth of order unity at a typical wave-length, $\lambda \cong 1\cdot 5\,\mu$. At $\lambda \cong \frac{1}{3}\mu$, in the ultra-violet, the optical depth to the same level in the atmosphere will be much greater, the increase being determined by the factor $(1 + 4\lambda^2)^{-1}$, just as in the case of interstellar reddening—the increase is by a factor ~ 7. Hence the ultra-violet emission must come from a higher

level than the layers contributing to the main emission at $\lambda \simeq 1 \cdot 5 \mu$. Since the ultra-violet intensity is very sensitive to temperature for these cool stars, and since the temperature at the higher level is likely to be less than the effective temperature, an exceptionally low emission in the ultra-violet is to be expected, and is indeed found in these stars (**16, 17**).

5. *The condensation of carbon grains at stellar surfaces.*—Apart from the carbon associated with oxygen in CO, most of the carbon is free, existing as gas (monatomic and polyatomic) and possibly as carbon grains. It is true that the dissociation energy of CN is high, $\sim 8 \cdot 3$ eV, but except under conditions of strong nitrogen excess—not contemplated here—nitrogen does not compete seriously for carbon, because of the even higher dissociation energy of N_2, $\sim 9 \cdot 9$ eV. (The situation is otherwise for oxygen, $C + O \rightarrow CO + 11 \cdot 2$ eV, $O + O \rightarrow O_2 + 5 \cdot 25$ eV.) Our problem is therefore to consider the distribution of free carbon, it being supposed that there is an excess of C over and above that combined with O.
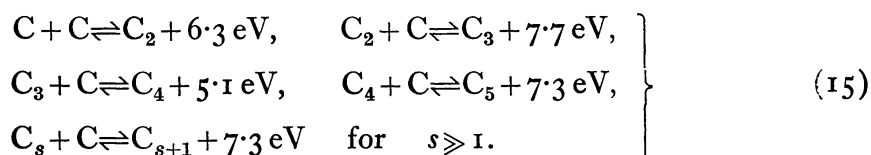
Equilibrium for the reaction

$$C_s + C \rightleftharpoons C_{s+1} + Q(s), \tag{13}$$

is expressed by

$$\frac{n_{s+1}}{n_s n} = A(s) \cdot \frac{h^3}{(2\pi m k T)^{3/2}} \cdot 10^{(5 \cdot 04/T_3)Q(s)} \tag{14}$$

where n_s is the number density of C_s; n, m are the number, density and mass of monatomic carbon; T_3 is the temperature in units of 10^3 °K and $Q(s)$ is in eV. The quantity $A(s)$ contains a factor of order unity arising from the weights of the ground states of C, C_s, C_{s+1}, and from the masses of the constituents. It also contains the ratio of the partition functions for C_{s+1} and C_s. This ratio is of order unity except in the case $s = 1$—i.e. for $C + C \rightleftharpoons C_2 + 6 \cdot 3$ eV—when the partition function for the C_2 molecule gives $A(1) \simeq 10^3$. The other quantities in (14) play a more decisive role. For $T \simeq 2500$ °K, $h^3/(2\pi m k T)^{3/2} \simeq 10^{-27}$ cm^3. Evidently the value of $Q(s)$ is crucial in deciding the balance of (13). The following data concerning Q values are available (**14**):

$$\left.\begin{array}{ll} C + C \rightleftharpoons C_2 + 6 \cdot 3 \text{ eV}, & C_2 + C \rightleftharpoons C_3 + 7 \cdot 7 \text{ eV}, \\[4pt] C_3 + C \rightleftharpoons C_4 + 5 \cdot 1 \text{ eV}, & C_4 + C \rightleftharpoons C_5 + 7 \cdot 3 \text{ eV}, \\[4pt] C_s + C \rightleftharpoons C_{s+1} + 7 \cdot 3 \text{ eV} & \text{for} \quad s \gg 1. \end{array}\right\} \tag{15}$$

Applying (14) for r, s and eliminating n,

$$\frac{n(r+1)}{n(r)} = \frac{A(r)}{A(s)} 10^{(5 \cdot 04/T_3)[Q(r) - Q(s)]} \cdot \frac{n(s+1)}{n(s)}. \tag{16}$$

When $s \gg 1$ we have the case of bulk carbon, with $Q(s) = 7 \cdot 3$ eV. For carbon grains to be thermodynamically stable it is necessary that $n(s+1)/n(s)$ shall rise above unity. At the critical stage at which $n(s+1)/n(s) = 1$, $s \gg 1$, (16) gives

$$\frac{n(r+1)}{n(r)} = \frac{A(r)}{A(s)} \cdot 10^{(5 \cdot 04/T_3)[Q(r) - 7 \cdot 3]}, \tag{17}$$

which can be used for small values of r. Except in the case $r = 1$, $A(r)/A(s)$ is of order unity, so that $n(r+1)/n(r)$ is determined essentially by $Q(r)$. Where $Q(r)$ is low, as it is for $C_3 + C \rightleftharpoons C_4 + 5 \cdot 1$, $n(r+1)/n(r) \ll 1$. For example,

$n(4)/n(3) \cong 10^{-5}$ at $T_3 = 2\cdot2$. It is the existence of "gaps" such as this in the building chain that leads to condensation into grains of appreciable size, instead of into a much larger number of very small nuclei. We shall return to this point in a later section.

For $r = 1$, $A(r)/A(s) \cong 10^2$, $Q(r) = 6\cdot3$ eV, and n_2/n is of order unity in spite of $Q(r)$ being less than $Q(s)$ by 1 eV. This exceptional case arises from the large ratio of the partition functions of C_2 and C. We see therefore that under conditions where bulk carbon is thermodynamically stable, equilibrium in $C + C \rightleftharpoons C_2 + 6\cdot3$ requires an appreciable fraction of the gaseous carbon to exist as C_2. Also, since $Q(2) = 7\cdot7$ eV, which is greater than $Q(s) = 7\cdot3$ eV, $n(3)/n(2) > 1$, and C_3 exists in strong concentration. Thereafter, the polyatomic concentrations fall away, because of the gap at C_4.

However, a question does arise concerning the establishment of equilibrium in $C + C \rightleftharpoons C_2 + 6\cdot3$ eV. This particular reaction comes to equilibrium more slowly, by a factor $\sim 10^6$, than succeeding steps in the building chain. For a pulsating star with T variable this slowness of response causes n_2/n to be always out of step with its thermodynamic value, particularly near minimum phase when the absolute value of n is probably less than 10^{10} cm^{-3}. Each C atom then experiences no more than 1 collision per second with other carbon atoms. But only a fraction $\sim 10^{-10}$ is associative. Hence a time of order 10^{10} sec is required to establish equilibrium, and this is much longer than the pulsation period.

If a star is losing carbon into space the problem of estimating the polyatomic concentrations is still more difficult. In this case carbon is resupplied to the atmosphere by convection from below. It is necessary then to know how long a particular sample remains in the atmosphere. If the atmospheric carbon is renewed at every pulsation period there would probably not be sufficient time to establish the concentrations of C_2, C_3 at their equilibrium values and n_2, n_3, instead of becoming comparable to, or even greater than, n, would remain perhaps ten to a hundred times less than the equilibrium values.

Strictly, it is not possible to calculate the conditions under which bulk carbon becomes stable unless either C_2 is in equilibrium with C or the ratio $n(2)/n$ is specified. However, unless very precise results are required, this uncertainty is unimportant. The conditions under which carbon grains condense in monatomic carbon vapour are closely similar to the conditions for condensation in a vapour in which C, C_2, C_3 are in equilibrium. The reason for this is that the equilibrium concentrations of C, C_2, C_3 are comparable with each other. It will therefore be sufficient to consider the formation of grains in a monatomic vapour. Values for the pressure of such a vapour in equilibrium with graphite crystals are given in the following table. They are obtained from the formulae set out in the Appendix, using essentially $Q(s) = 7\cdot3$ eV, $s \gg 1$.

<div align="center">

TABLE II

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$T(°K)$	Vapour pressure (dyne cm^{-2})	T	Vapour pressure
1500	$1\cdot7 \times 10^{-12}$	2300	$1\cdot2 \times 10^{-3}$
1600	$6\cdot6 \times 10^{-11}$	2400	$6\cdot0 \times 10^{-3}$
1700	$1\cdot7 \times 10^{-9}$	2500	$2\cdot6 \times 10^{-2}$
1800	$2\cdot7 \times 10^{-8}$	2600	$1\cdot0 \times 10^{-1}$
1900	$3\cdot6 \times 10^{-7}$	2700	$3\cdot7 \times 10^{-1}$
2000	$3\cdot7 \times 10^{-6}$	2800	$1\cdot2$
2100	$3\cdot1 \times 10^{-5}$	2900	$3\cdot5$
2200	$2\cdot1 \times 10^{-4}$	3000	$9\cdot6$

At first sight it might seem easy to estimate a value of T below which carbon vapour would condense extensively into grains. If the surface opacity requires an effective contribution from H^- (molecular bands do not cover the whole spectrum) the photospheric hydrogen density N, for giants with $T < 3000\,°K$, must be about 10^{15} atom cm^{-3}. Hence with $x = n/N$ not less than 10^{-3} for the carbon stars, $n > \sim 10^{12}$ atom cm^{-3}, and the partial pressure of carbon vapour at the temperatures in question ~ 0.3 dyne cm^{-2}. When $T < \sim 2700\,°K$, this exceeds the vapour pressure of graphite, and so we might expect an extensive condensation of carbon grains as soon as T falls below $\sim 2700°\,K$ during a stellar pulsation. However, the estimate $N \cong 10^{15}\,cm^{-3}$, based on absorption by H^-, ceases to be valid as soon as carbon grains begin to form even in small quantity, because of the large mass absorption coefficient of the grains themselves. We must therefore proceed more carefully.

In Section 2 we obtained $1.28 \times 10^5 (1 + 4\lambda^2)^{-1}\,cm^2\,gm^{-1}$ for the mass absorption coefficient of grains. The mass of carbon per unit volume is xNm. Suppose a fraction y is condensed as grains, then the absorption *per* cm^{-3} is $1.28 \times 10^5 xyNm(1 + 4\lambda^2)^{-1}$. Multiplying by the scale height $\sim kT/2gM$, where M is the mass of the hydrogen atom and g is surface gravity (the 2 appears because the hydrogen is largely molecular), we obtain the following surface condition

$$1.28 \times 10^5 xyNm(1 + 4\lambda^2)^{-1} \cdot \frac{kT}{2gM} \cong 1. \tag{18}$$

The partial pressure P_c of carbon vapour is $xN(1-y)kT$. Using (18) we therefore obtain for P_c

$$P_c = g\frac{M}{m}\frac{1-y}{y} \cdot \frac{1 + 4\lambda^2}{6.4 \times 10^4}. \tag{19}$$

With $\lambda = 1.5\,\mu$ as a typical wave-length, $M/m = 1/12$, $g \cong 1\,cm\,sec^{-2}$ for a giant star,

$$P_c \cong 10^{-5}\frac{1-y}{y}\,dyne\,cm^{-2}. \tag{20}$$

In accordance with the above discussion, grains form when T falls below $\sim 2700\,°K$. But at first, $y \ll 1$. As T continues to fall, y increases towards unity. The value of y appropriate to a particular T is given by equating P_c to the vapour pressure of graphite. The vapour pressure values of Table II show that T must fall to $\sim 2000\,°K$ before y increases to 0.5—i.e. before half the carbon is condensed. It is emphasized that y is independent of $x = n/N$, the carbon concentration relative to hydrogen.

These considerations show that the process of grain formation possesses negative feed-back. The opacity of the grains reduces the photospheric density, which reduces P_c, and hence moderates the process.

The total number of carbon atoms lying above the photosphere is $\sim P_c/2gM \cong 3 \times 10^{23} P_c\,cm^{-2}$, for $g \cong 1\,cm\,sec^{-2}$. The number of C_2 molecules is of a similar order, as was seen above.

6. *The escape of grains from the atmosphere of a star.*—The outward radiation pressure P acting on a grain is obtained by multiplying the flux of radiation,

$\frac{1}{4}\alpha c T^4$, where α is Stefan's constant, by $\pi a^2 Q(a, \lambda)/c$, with Q taken at some typical wave-length. Thus with Q given by (6), we have

$$P = \frac{3\pi^2}{4} \frac{a^3 \sigma \alpha T^4}{c(1 + 4\lambda^2)} \simeq 6 \times 10^3 a^3, \tag{21}$$

where $T = 2300\ ^\circ\text{K}$, $\sigma = 1\cdot2 \times 10^{15}\ \text{sec}^{-1}$, $\lambda = 1\cdot5\ \mu$, have been used in the numerical reduction. The inward gravitational force is given by $\frac{4}{3}\pi a^3 sg \simeq 9a^3$, for $g \simeq 1\ \text{cm sec}^{-2}$. The outward radiation pressure is therefore much greater than gravity, and grains tend to be repelled away from the star.

However, the grains are not at first repelled freely. They are immersed in the photospheric gases which produce a drag as the grains move outwards. The drag force F on a spherical grain is

$$F = 6\pi a \eta u, \tag{22}$$

where u is the relative speed between the grain and the gas, and η is the viscosity, given by

$$\eta \simeq \tfrac{1}{2} a M N \left(\frac{kT}{\pi M}\right)^{1/2}. \tag{23}$$

Numerically,

$$F \simeq 4 \times 10^{-18} a^2 N u. \tag{24}$$

The grain accelerates so long as P exceeds F. Eventually, however, u becomes so large that $F \simeq P$. At this stage the frictional resistance of the gas prevents a further increase of u, so long as the grain remains within the photospheric layers. The maximum speed with which the grain can move upwards through the first scale height is therefore given by equating F and P,

$$u \simeq 1\cdot5 \times 10^{21} a N^{-1}\ \text{cm sec}^{-1}, \tag{25}$$

and the time τ required for this is $kT/2Mgu$,

$$\tau \simeq 6 \times 10^{-11} a^{-1} N\ \text{sec}. \tag{26}$$

The time required for the grain to move upward through the second scale height is less than (26) by a factor e, since the hydrogen density N falls off exponentially with height above the photosphere. It is the first scale height therefore that determines the time scale required for the grains to diffuse upward out of the star's atmosphere.

If the value of τ, computed for the smallest value of N arising in the pulsation cycle, and for the radius a attained by the grains, were greater than the pulsation period of the star then any appreciable escape of grains would be prevented by the frictional drag. This follows because towards maximum phase of the cycle the grains must be wholly, or largely, evaporated. Grains condensing near minimum phase must escape at that phase if they are to leave the star. Since the stars in question have pulsation periods of several hundred days, we can reasonably take 10^7 sec as the time scale allowed for the escape—i.e. we require $\tau < \sim 10^7$ sec. Putting $a \simeq 10^{-5}$ cm, we therefore obtain the following condition on the photospheric hydrogen density

$$N < \sim 1\cdot6 \times 10^{12}\ \text{atom cm}^{-3}, \tag{27}$$

if escape is to take place.

This rather low value would not be attained but for the opacity produced by the grains themselves. This is large enough to reduce the photospheric density sufficiently for (27) to be satisfied, provided the effective temperature falls below about 2300 °K, as it does in many stars. Writing x for the abundance of carbon relative to hydrogen, we have

$$ xN = \frac{P_c}{kT} \cdot \frac{1}{1-y} \simeq \frac{10^{-5}}{kT} \cdot \frac{1}{y} \simeq 3 \times 10^7 y^{-1}, \tag{28} $$

using (20) for P_c, and remembering that y is the fraction of carbon that is condensed into grains. Hence (27) can be expressed as a condition on y,

$$ y > \sim 2 \times 10^{-5} x^{-1}. \tag{29} $$

In solar material $x \simeq 5 \times 10^{-4}$. A higher value is to be expected in the carbon stars, perhaps $x \simeq 2 \times 10^{-3}$, in which case we require $y > \sim 10^{-2}$. Inserting in (20) we see that P_c must then be less than $\sim 10^{-3}$ dyne cm^{-2}. Reference to Table II shows that this requirement will be met if T falls below ~ 2300 °K. Carbon grains can be considered to leave the star's atmosphere provided the effective temperature falls below ~ 2300 °K for a time of order 10^7 seconds in each pulsation cycle.

A point concerning surface gravity g is worth mentioning. The particular value $g \simeq 1$ cm sec^{-2} was used above to obtain the scale height $kT/2Mg \simeq 10^{11}$ cm. If g had been left in the calculation, (26) would have taken the form $\tau \simeq 6 \times 10^{-11} a^{-1} g^{-1} N$ sec. The value $g \simeq 1$ cm sec^{-2} was also used in obtaining (20) from (19). If g had been left in that calculation, (20) would have read $P_c \simeq 10^{-5}(1-y)gy^{-1}$, and (28) would have become $xN \simeq 3 \times 10^7 gy^{-1}$, so that $\tau \simeq 2 \times 10^{-3} a^{-1} y^{-1}$, irrespective of the value of g. With $a = 10^{-5}$ cm, $\tau < 10^7$ sec, we again obtain (29). The precise value of surface gravity has no effect on the result of the present section.

7. *The outward journey of a grain.*—Still another condition must be satisfied if a grain is to reach interstellar space. Once clear of the parent star's atmosphere no further condensation of vapour on to the grain can take place. The grain is then exposed to the star's radiation field. Evaporation will take place unless the grain is repelled away in a sufficiently short time.

To decide the time scale for evaporation of a grain of radius a it is useful to consider the converse process of condensation without evaporation. The number of carbon atoms striking a grain per unit time in an atmosphere of partial pressure P_c is $4\pi a^2 P_c/(2\pi mkT)^{1/2}$. Writing f for the accommodation coefficient, the rate of increase of mass in the absence of evaporation is

$$ 4\pi a^2 f P_c \left(\frac{m}{2\pi kT} \right)^{1/2}. \tag{30} $$

Since the rate of increase of mass can also be written as $4\pi a^2 s(da/dt)$ we have

$$ \frac{da}{dt} = f \frac{P_c}{s} \left(\frac{m}{2\pi kT} \right)^{1/2}, \tag{31} $$

and the time t required for the growth of the grain is

$$ t = \frac{sa}{f P_c} \left(\frac{2\pi kT}{m} \right)^{1/2}. \tag{32} $$

With the value $f = 10^{-3}$ given by Doehaerd, Goldfinger and Waelbroek,

$$t \simeq 10^9 a P_c^{-1} \text{ sec.} \tag{33}$$

If P_c is taken as the vapour pressure of solid carbon, this result also gives the time of evaporation. As T falls below 2300 °K, P_c becomes less than 10^{-3} dyne cm^{-2}, so that, for $a \simeq 10^{-5}$ cm, the time of evaporation exceeds 10^7 sec. If a grain can "get away" from the star in less than this interval it can be considered to have escaped to interstellar space. To get away from the star in the present sense it is by no means necessary for the grain to move very far from the star. Since the vapour pressure of bulk graphite falls steeply with temperature (see Table II) the grain already becomes quite stable against evaporation at the stage where its distance r from the star's centre is twice (say) the photospheric radius R. And the time required for r to reach $2R$ is much less than 10^7 sec, as will now be shown.

Once clear of the photospheric gases, a grain is subject to an outward acceleration $P/\frac{4}{3}\pi a^3 s$, so that

$$\ddot{r} = \frac{3P}{4\pi a^3 s} \simeq 6 \times 10^2 \left(\frac{R}{r}\right)^2, \tag{34}$$

where the radiation pressure $P \simeq 6 \times 10^3 a^3 (R/r)^2$ is obtained by multiplying the photospheric radiation pressure, given in (21), by $(R/r)^2$ to allow for the falling intensity of radiation as r increases above R. Integrating

$$\dot{r}^2 \simeq 1200 R \left(1 - \frac{R}{r}\right), \tag{35}$$

and the time taken for r to increase to $2R$ is

$$\frac{1}{20\sqrt{3R}} \int_R^{2R} \left(\frac{r}{r-R}\right)^{1/2} dr = \frac{R^{1/2}}{20\sqrt{3}} \left[\sqrt{2} + \ln (1 + \sqrt{2})\right]. \tag{36}$$

With $r \simeq 3 \times 10^{13}$ cm, this is only $\sim 3 \times 10^5$ sec, considerably less than the available time.

The limiting velocity as $r \to \infty$ of a grain takes the very high value of ~ 2000 km sec^{-1}, as can be seen by putting $R \simeq 3 \times 10^{13}$ cm in (35). In spite of this high speed a grain of radius 10^{-5} cm would be slowed appreciably by collisions with the interstellar gas after travelling a distance $\sim 10^{19}$ cm. This is less, but not greatly less, than the width of the interstellar medium. The possibility therefore arises that, in galaxies containing less gas than our own, carbon grains might be expelled entirely from the galaxies. In this connection it may be relevant that cases are known of whole galaxies being surrounded by vast aggregations of dust.

8. *The size of carbon grains.*—In the above work it was considered that grains would form if the partial pressure of gaseous carbon were to exceed the vapour pressure of bulk graphite by only a small margin. At the partial pressures, and for the time scales in question, this assumption is probably not strictly correct; for it is likely that condensation nuclei, containing perhaps twenty or thirty carbon atoms, do not form at an adequate rate unless P_c, the partial pressure, exceeds the vapour pressure of the bulk crystal by a moderate factor at least.

Consider grains forming as T falls below 2300 °K, the critical situation so far as the escape of grains is concerned. The above work shows that $N \sim 1 \cdot 6 \times 10^{12}$ cm^{-3}, so that with x, the abundance of carbon relative to hydrogen, of order 2×10^{-3} the density of gaseous carbon atoms is $\sim 3 \times 10^9$ cm^{-3}. At this density each nucleus C_r, r in the range 2 to 20, say, experiences of the order of 1 collision with a carbon atom every second. The fraction of collisions leading to attachment, $C_r + C \rightarrow C_{r+1}$, is probably no more than 10^{-5}, less than the accommodation coefficient for bulk carbon. Hence in 10^7 sec there are of the order of 10^2 associative collisions (for each value of r). This would be sufficient to build more than an adequate number of condensation nuclei if there were no inverse reactions taking place, $C_{r+1} \rightarrow C_r + C$. However, for some values of r the inverse reactions take place much more rapidly than the associative reactions. These are the gaps already mentioned in Section 5.

The case $C_3 + C \rightleftharpoons C_4 + 5 \cdot 1$ eV is an example. The equilibrium balance discussed in Section 5 gave $n_4/n_3 \simeq 10^{-5}$, implying that the time required for $C_4 \rightarrow C_3 + C$ is less by 10^{-5} than the time for $C_3 + C \rightarrow C_4$. Since the latter must be comparable with the next building step, $C_4 + C \rightarrow C_5$, it follows that only one associative building of C_4 in 10^5 continues to C_5—the others simply dissociate back to $C_3 + C$. Hence we have a situation in which $C_3 + C \rightarrow C_4$ occurs about 10^2 times for each C_3 molecule during the available time, and that on each occasion there is a chance $\sim 10^{-5}$ of the building going on to C_5. It follows that in total a fraction $\sim 10^{-3}$ of the C_3 goes on to C_5. A similar situation occurs for each such gap. Three or four gaps in the building of C_r, $r \simeq 20$, leads to a very slow rate of formation of condensation nuclei. The rate can be much increased, however, by allowing the temperature to fall, so that the partial pressure P_c rises above the vapour pressure of the bulk crystal. The rate of the dissociative reactions is then slowed according to the factor $10^{-(5 \cdot 04/T_3) Q(r)}$, whereas the rate of the associative reactions is hardly changed. Suppose, for example, that there are three gaps each with a Q of 5 eV. The rate at which each gap is crossed increases as $10^{25 \cdot 2/T_3}$ and the rate at which all three gaps are crossed increases as $10^{75 \cdot 6/T_3}$. A quite modest reduction of temperature therefore produces a very marked increase in the rate of formation of nuclei.

We saw above that the opacity of the grains produces a negative feed-back. In the absence of the grain opacity the value of P_c would greatly exceed the vapour pressure of bulk carbon. This forces grains to condense, and the grains then change the photospheric density, causing P_c to fall, and thereby cutting back the condensation. The balance of these effects is expressed by equation (20). We also argued that y, the fraction of condensed carbon, appropriate to a specified T, is determined on equating P_c in (20) to the vapour pressure of bulk graphite. Now we see that this condition must quite probably be refined. The value of y depends on the rate of formation of condensation nuclei. Formally, we can write $y = y(P_c, T)$, the functional dependence on P_c, T being determined by considerations of the sort described in the previous paragraph. Together with (20), we then have y as a function of T.

However, because the rate of formation of condensation nuclei depends very sensitively on T it is unlikely that this more accurate consideration would yield a dependence of y on T appreciably different from that given in Section 5. The situation is that T must very likely be lower than the value at which P_c equals the vapour pressure of bulk graphite, but only a little lower.

Two important points arise out of these rather complicated considerations. We have already pointed out that if condensation nuclei formed very readily a large number of tiny grains would be formed. It is because the control of grain formation lies in a regulation of the number of nuclei that are allowed to form that comparatively large grains are produced. Indeed, with P_c now greater than the vapour pressure of bulk carbon, the rate at which grains are built is determined by (31). Inverting (33), and putting $t \cong 10^7$ sec for the time scale, we have

$$a \cong 10^{-2} P_c \text{ cm}. \tag{37}$$

For the grains to escape (29) must be satisfied, i.e. $y > \sim 10^{-2}$, and with this value in (20), $P_c < 10^{-3}$ dyne cm^{-2}. Inserting in (37) gives $a < \sim 10^{-5}$ cm.

9. *The rate of emission of carbon grains from stars.*—It is easy to estimate the rate of emission of carbon grains. The grains are emitted when the photospheric hydrogen density falls below $\sim 1 \cdot 6 \times 10^{12}$ cm^{-3}. For $x = 2 \times 10^{-3}$, the carbon density before emission is $\sim 3 \times 10^9$ cm^{-3}, giving a mass $\sim 6 \times 10^{-14}$ gm cm^{-3}. Over a scale height of $\sim 10^{11}$ cm the carbon content of the atmosphere is $\sim 10^{-3}$ gm cm^{-2}. If now we consider a star of bolometric magnitude -5, appropriate for an N star, and of effective temperature 2000 °K, the photospheric area is $\sim 5 \times 10^{28}$ cm^2. The total mass of atmospheric carbon, at the pulsation stage where T falls towards 2000 °K, is therefore $\sim 5 \times 10^{25}$ gm. If this carbon, or an appreciable fraction of it, escapes during the minimum phase of the pulsation cycle, the loss is $\sim 5 \times 10^{25}$ gm per cycle—about 5×10^{25} gm per year per star. With $\sim 10^4$ such stars in the Galaxy the mass of carbon grains produced per year is $\sim 5 \times 10^{29}$ gm. Distributed throughout the volume of the interstellar medium, $\sim 10^{66}$ cm^3, the rate is $\sim 5 \times 10^{-37}$ gm cm^{-3} year^{-1}. In $\sim 3 \times 10^9$ years this gives the required interstellar density of 3×10^{-27} gm cm^{-3} within a small factor.

The 10^4 N stars appear to be sufficient. The reason lies in the huge surface areas of these stars. The R stars have much smaller surface areas and are much less effective in the production of grains.

APPENDIX

It was pointed out in Section 5 that bulk carbon may be expected to condense extensively in a stellar atmosphere when the partial pressure of free carbon vapour exceeds the saturation vapour pressure of carbon crystal. The first step in investigating the condensation of carbon crystals must therefore be to estimate the saturation pressure. We proceed, quite generally, to derive an expression for the vapour pressure of any simple crystal.

Consider an assembly of atoms in a volume V, a large preponderance of which are in the condensed state at absolute temperature T. The number $\bar{N}$ of free atoms in equilibrium with the condensed solid at temperature T is given by (18)

$$\bar{N} = g(T)/\kappa(T), \tag{38}$$

where $g(T)$, $\kappa(T)$ are the partition functions of a free and bound atom respectively. The saturation pressure p_s is given by

$$p_s = \bar{N}kT/V. \tag{39}$$

Choosing the zero of energy as that appropriate for the atoms at infinite separation and taking the atoms as structureless mass points we have $g(T)$ and $\kappa(T)$ given to a satisfactory approximation by (19)

$$g(T) = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot V,\qquad (40)$$

and,

$$\ln \kappa(T) = \frac{\chi}{kT} - 9\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \ln(1 - e^{-x}) \cdot x^2\, dx,\qquad (41)$$

where $m =$ mass of an evaporated atom, $k =$ Boltzmann's constant, $h =$ Planck's constant, $\chi =$ heat of evaporation of an atom from absolute zero, $\Theta =$ Debye temperature of the solid. The integral appearing in (41) may be integrated by parts, giving

$$\int_0^{\Theta/T} \ln(1 - e^{-x}) \cdot x^2 dx = \frac{1}{3}\left(\frac{\Theta}{T}\right)^3 \left[\ln(1 - e^{-\Theta/T}) - \tfrac{1}{3}D\left(\frac{\Theta}{T}\right)\right],\qquad (42)$$

where

$$D(x) = \frac{3}{x^3} \int_0^x \frac{t^3}{e^t - 1} dt.$$

$D(x)$ is the well-known Debye function and is obtainable from tables. (For $x \approx 0$ it can be shown that $D(x) \approx 1 - 3x/8$.) Equations (38) to (42) now yield

$$p_s = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot kT \cdot (1 - e^{-\Theta/T})^3 \cdot \exp\left[-D\left(\frac{\Theta}{T}\right)\right] \cdot \exp -\frac{\chi}{kT}.\qquad (43)$$

When $\Theta/T \ll 1$ the integral (42) approximates to $\dfrac{1}{3}\left(\dfrac{\Theta}{T}\right)^3 \ln\left(\dfrac{\Theta}{T}\right)$ and we have

$$p_s = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot kT \cdot \left(\frac{\Theta}{T}\right)^3 \cdot \exp -\frac{\chi}{kT}.\qquad (44)$$

The condition $\Theta/T \ll 1$ is satisfied for most elements at $T \sim 2000$ °K, except for a very few, including carbon, which have high Debye temperatures. For graphite $\Theta = 2230$ °K, so that $\Theta/T \sim 1$ for $T \sim 2000$ °K. As we are concerned with numerical calculations relating to carbon, it is evidently preferable to retain the vapour pressure equation in the form (43). The quantity χ appearing in the exponential is the heat of evaporation in ergs per particle. Heats of evaporation are usually tabulated (14) as Q kilocalories per mole. Re-writing (43) in terms of Q, and substituting numerical values for h and k, we obtain

$$p_s = 2 \cdot 62 \times 10^4 \left(\frac{m}{m_H}\right)^{3/2} \cdot T^{5/2} \cdot (1 - e^{-\Theta/T})^3 \cdot \exp\left[-D\left(\frac{\Theta}{T}\right)\right] \cdot \exp\frac{-507Q}{T},\qquad (45)$$

where m_H is the mass of an H atom and Q is expressed in kilocalories per mole. The temperature is in degrees absolute. We now have an expression for the saturation vapour pressure of any element as a function of T.

For graphite we have the following data: $m/m_H = 12$, $\Theta = 2230$ °K, $Q = 171 \cdot 7$ kcal mole^{-1}. (The value $Q = 171 \cdot 7$ is correct at about 290 °K, not at absolute zero. The difference is a term due to the specific heat, viz., $\int_0^{290} C_v\, dT$, which is in general small compared to Q. Using the Debye approximation

$C_v = (12\pi^4 k/5)(T/\Theta)^3$, for small Θ/T, we find this difference in the case of carbon to be about 0.075 kcal mole^{-1}.)   Using the above data and evaluating the various quantities in equation (45) we arrive at the results set out in Table II.   It is seen that for the range of T in question, $\exp[-D(\Theta/T)]$, $(1 - e^{-\Theta/T})^3$ and $T^{5/2}$ are weak functions of T compared with the last exponential term which varies quite steeply.

St John's College,   *Trinity College,*
    Cambridge.   *Cambridge.*
1962 *June.*

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